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Effect of Aging on the Soundness of Regularly Hydrated Dolomitic Lime Putties

Lansing S. Wells, Walter F. Clarke, and Ernest M. Levin

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Foreword

The use of regularly hydrated dolomitic lime (type N-normal finishing), characterized by a high percentage of unhydrated magnesia, has been shown at the Bureau to result in extensive blister-type failures in white-coat plaster. The failures are caused by expansion in the white coat, accompanying delayed hydration of the magnesia. The Bureau cooperated in the development of methods for producing dolomitic limes so highly hydrated that expansion by further hydration would be negligible, and such limes are now available commercially. Unfortunately, in many instances unsound regularly hydrated dolomitic lime is still being used in the preparation of white coat.

The custom has been to soak regularly hydrated dolomitic finishing lime as a putty for 12 to 24 hours before using, in order to provide a plastic putty. That such a soaking period is insufficient to provide a sound lime putty, by additional hydration of MgO, is amply demonstrated by the prevalence of blister-type failures in white-coat plaster. Some believe, however, that extension of the soaking period somewhat would be sufficient to provide a sound lime putty.

This report shows that for the regularly hydrated dolomitic limes studied, the aging period necessary to produce a sound lime putty varied from a minimum of 3 weeks to over 32 weeks, an aging period altogether too long from a practical standpoint. Suitable alternates are discussed.

A. V. Astin, *Acting Director.*

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Lansing S. Wells, Walter F. Clarke, and Ernest M. Levin

Regularly hydrated dolomitic limes are potentially unsound because they contain unhydrated magnesia that may hydrate subsequently in the set plaster, causing disruptive expansion. It is important to know the time required to soak these limes as putties so that sufficient magnesia will have been hydrated to give a sound putty. The customary soaking period of 1 day is inadequate, as evidenced by the prevalence of white-coat expansion failures. Consequently, the progressive hydration of magnesia in dolomitic lime putties upon aging and the attendant decrease in autoclave expansion of cement-lime putty bars were studied for 18 regularly hydrated dolomitic limes representative of commercial production. The limes differed markedly in regard both to the time required to reach a given percentage of expansion and to the extent of hydration at the given expansion. The shortest time of aging required to reduce the expansion to 1 percent (a suggested specification limit for soundness) was 3 weeks, whereas the longest time was in excess of 32 weeks. When the expansion had been reduced to 1 percent, the proportion of total magnesia hydrated ranged from 83 to more than 97 percent. Inasmuch as long and variable aging periods are impractical, suitable alternates, including the use of newly developed sound hydrated limes, are discussed.

1. Introduction

Regularly hydrated dolomitic limes have been used extensively in the preparation of white-coat plaster. These finishing hydrated limes are desirable because they yield plastic putties, but undesirable because they are potentially unsound. The unsoundness arises from the fact that they contain magnesia (unhydrated magnesium oxide) which may hydrate subsequently (forming magnesium hydroxide) in the set plaster and thereby disruptive expansion may result. Extensive failures of white-coat plaster caused by this type of expansion are described in Building Materials and Structures Report 121 [1].[1]

Until recently, in the commercial hydration of dolomitic limes, which contain calcium oxide (CaO) and magnesia (MgO) in nearly equimolar ratio, the CaO was almost invariably hydrated, whereas the MgO was only slightly hydrated. Wells and Taylor [2] in 1937 developed heat-of-solution and ignition-loss methods for determining the degree of hydration of magnesia in hydrated dolomitic limes and putties. They showed that for six regularly hydrated dolomitic limes, as received from the manufacturers, an average of only 12.5 percent of the total magnesia was hydrated.

More recently, in a study of the expansive characteristics of hydrated limes and the development of an autoclave test for soundness, Wells, Clarke, and Levin [3] showed that for 27 hydrated limes of this type, an average of 15.7 percent of the total magnesia was hydrated. Calculations based on the analyses of 185 regularly hydrated dolomitic limes submitted to the Bureau for test from 1923 to 1940 indicated that the average was 17.0 percent [1].

Manufacturers of regularly hydrated dolomitic finishing limes almost invariably recommended that the putty be used only following a 12- to 24-hour soaking period. An erroneous belief seemed to be prevalent that such a soaking period was sufficient not only to provide a plastic putty but at the same time to hydrate the product completely. However, Wells and Taylor [2] showed that for six of these hydrated limes the average percentages of total MgO hydrated in the putties at the end of 1, 3, and 7 days were only 19.1, 30.2, and 40.9, respectively. It is evident that if these values be representative of the behavior of regularly hydrated dolomitic lime, then the customary procedure of soaking the lime as a putty for 1 day must leave the bulk of the MgO still unhydrated and the product unsound.

Consequently, the primary purpose of the present investigation was to determine whether a potentially unsound regularly hydrated dolomitic lime can be rendered sound by soaking as a putty for a reasonable length of time and to point out to the architect, engineer, plastering contractor, plasterer, and others concerned with plastering the types of lime that will give satisfactory performance.

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[1] Figures in brackets indicate the literature references at the end of this paper.

2. Scope

To procure a fair cross section of the regularly hydrated dolomitic limes being produced in the United States, 18 samples were obtained from separate lime producing centers.

The samples were analyzed chemically, and from the oxide composition the percentages of hydrated and unhydrated magnesia at the start were calculated.

The limes were then made into putties and stored under controlled conditions. At definite time intervals, a sample of each putty was mixed with portland cement and cast into a bar. The autoclave expansion of the hardened bar was determined subsequently. In this way, it was possible to ascertain the length of time required to soak the hydrated dolomitic lime as a putty in order that the magnesia be sufficiently hydrated so that the autoclave expansion would be no greater than 1 percent. One-percent expansion has been proposed as a specification limit for soundness of hydrated limes [3].

At the same time intervals, a sample of each putty was analyzed and the percentages of hydrated and unhydrated magnesia were calculated. From these data the progress of the hydration was followed. Equations were derived for making these calculations.

This information served as a basis for determining the relation between the autoclave expansion values and the percentages of unhydrated oxide in the putty at each time interval. Studies were also made of the relation between the autoclave expansion values and the reactivities of the MgO as reflected in the fineness of the hydrated products.

3. Materials

3.1. Hydrated lime

The 18 regularly hydrated dolomitic limes (also designed as type N—normal finishing hydrated lime [4]) were part of the group of hydrated limes used in the study "Expansive Characteristics of Hydrated Limes and the Development of an Autoclave Test for Soundness", RP1917 [3]. Thus, for convenience of identification and comparision, the limes in the present paper have been assigned the same numbers as in RP1917.

The oxide compositions of the selected limes were available from the previous investigation, but because of aeration caused by frequent handling and the fact that the storage containers were not completely airtight, it was deemed advisable to check the limes for additional hydration and carbonation. Inasmuch as the proportions of the different oxides remaining in the ignited limes could not change with time, only CO_2 and ignition-loss determinations were required as a basis for recalculating the compositions.

The chemical analyses, with the exception of the free-water determination, were made originally in accordance with Federal Specification SS–L–351 for hydrated lime [5; see also 6]; and the percentages of hydrated and unhydrated oxides were calculated in accordance with Proposed Amendment 1 [7; see also 6] to this specification.[2]

The adjusted oxide compositions recalculated on the basis of the new values for the ignition loss and CO_2 are given in table 1, columns 2 to

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[2] Recently, Levin [8] has presented two nomograms from which the compound composition of a hydrated lime can be easily and rapidly determined from the oxide analysis, thus saving time and labor of calculation.

TABLE 1. *Chemical analyses and calculated percentages of hydrated magnesia and unhydrated oxide for 18 regularly hydrated dolomitic limes, together with the ignition losses (after drying) of aged putties made from these limes*

Lime	Free water (volatile at 150° C)	Oxide composition (after drying at 150° C)							Calculated hydrated magnesia	Calculated unhydrated oxide [a]	Ignition loss of dry hydrated lime at start [b]	Ignition loss of putty dried at 150° C after aging for (time in weeks)—									
		Combined H_2O	CO_2	SiO_2	R_2O_3	CaO	MgO	Total				1/7	3/7	1	2	4	8	12	16	20	32
1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22
	%	%	%	%	%	%	%	%	%	%	%	%	%	%	%	%	%	%	%	%	%
23	0.48	18.34	1.64	1.75	1.07	45.21	31.85	99.86	10.05	21.80	19.98	20.27	20.98	21.55	22.23	23.25	24.69	25.51	26.06	26.62	26.66
24	.53	17.60	2.31	0.82	0.36	52.86	25.93	99.88	3.50	22.43	19.91	20.36	20.61	21.58	22.76	24.57	26.17	26.65	26.95	------	------
27	.45	18.68	0.56	.93	.36	46.51	32.94	99.98	8.88	24.06	19.24	20.22	21.10	22.37	23.79	25.21	26.43	26.99	26.94	------	------
28	.42	18.01	2.03	.12	.16	46.82	32.68	99.82	8.42	24.26	20.04	20.03	20.72	22.14	23.39	24.76	26.06	26.60	26.86	26.95	------
29	.49	16.24	5.81	.19	.17	45.80	31.70	99.91	8.64	23.06	22.05	22.85	23.68	24.77	25.75	26.95	28.10	28.43	28.66	28.73	------
30	.46	18.16	1.49	.28	.22	47.22	32.37	99.74	8.05	24.32	19.65	20.57	21.69	22.82	23.92	25.29	26.57	26.88	27.10	27.17	------
31	.42	17.61	1.73	.14	.14	47.01	33.31	99.94	7.19	26.12	19.34	20.03	20.60	21.99	23.62	25.53	26.96	27.34	27.53	------	------
34	.37	16.65	1.76	.40	.28	47.41	33.48	99.98	4.79	28.69	18.41	19.41	20.74	22.51	24.20	25.88	27.20	27.42	27.62	------	------
35	.25	17.16	1.61	.34	.22	47.18	32.80	99.31	5.95	26.85	18.77	19.60	19.96	21.00	22.13	23.38	25.01	25.77	26.13	26.25	26.63
37	.43	18.30	1.13	.20	.18	46.68	33.41	99.90	8.43	24.98	19.43	20.28	21.92	23.41	24.93	26.27	27.14	27.26	27.51	------	------
38	.27	16.60	0.98	.20	.10	48.43	32.98	99.29	3.22	29.76	17.58	17.92	18.79	19.77	20.68	22.00	23.94	25.19	25.72	25.97	26.47
40	.42	16.84	1.30	.20	.12	47.59	33.92	99.97	4.66	29.26	18.14	18.40	19.74	21.17	22.98	25.16	26.82	27.14	27.43	27.36	------
43	.39	16.50	1.31	.18	.16	47.85	34.00	100.00	3.70	30.30	17.81	18.44	19.28	21.20	23.55	25.91	27.49	27.81	27.86	------	------
44	.48	16.88	1.13	.79	.53	47.20	33.32	99.85	4.87	28.45	18.01	18.93	19.20	20.14	21.47	23.58	25.69	26.48	26.91	27.06	------
45	.50	16.19	1.45	.10	.12	46.81	35.23	99.90	3.90	31.33	17.64	18.84	20.31	23.26	25.58	27.11	27.80	27.86	28.00	------	------
46	.28	16.06	1.05	.14	.18	48.26	34.25	99.94	2.20	32.05	17.11	18.03	18.44	19.78	21.23	23.42	25.72	26.58	26.95	27.15	------
47	.48	16.03	0.80	1.42	.46	47.53	33.70	99.94	2.43	31.27	16.83	17.30	17.90	19.36	21.59	24.03	26.06	26.68	26.72	26.75	------
48	.53	14.63	1.69	1.34	.68	48.28	32.99	99.61	[c] 0.00	[c] 33.59	16.32	17.12	16.99	17.94	19.92	23.35	25.89	26.44	26.70	26.80	26.86

[a] Equal to the total MgO (column 8) minus the hydrated MgO (column 10).
[b] Equal to the sum of columns 3 and 4.
[c] Calculations for this lime showed all MgO (column 8) and 0.6% of CaO as unhydrated (column 11).

9, inclusive. The recalculated percentages of hydrated and unhydrated oxides are shown in columns 10 and 11, respectively.

The arrangement of limes, column 1, follows the numerical sequence recorded in RP1917, in which publication the sequence was based on the order of increasing percentage of calculated unhydrated oxide. Inspection of column 11 shows some deviations from the percentage sequence. It is apparent, therefore, that the limes had undergone additional hydration and carbonation of variable amount.

3.2. Cement

One brand of portland cement was used in this investigation. It conformed to type 1 of Federal Specification SS–C–192 [9], and was designated as cement No. 10 in RP1917. The autoclave expansion of the cement alone was 0.11 percent.

4. Procedure and apparatus

4.1. Preparation and storage of putty

Approximately 2,250 g of hydrated lime was weighed into a glass jar. Water was added slowly with constant stirring until a smooth plastic mix was obtained. The aim was to approximate an on-the-job mortar-box consistency. The jar then was sealed with a screw-on cap. The percentages of water in the putties as prepared varied from a minimum of 44.4 (for lime 29) to a maximum of 51.1 (for lime 45), with an average value of 47.5. During the entire investigation, jars were stored in a constant-temperature room maintained at 21° ±1° C (70° ±2° F).

The putties were tested over a maximum period of 32 weeks, according to the following schedule: After aging (in weeks) 1/7, 3/7, 1, 2, 4, 8, 12, 16, 20, and 32. At these time intervals, sufficient putty was removed for the determinations of (1) free water in the putty, (2) ignition loss of the resultant dried putty, and (3) autoclave expansion of cement-lime bars made from the putty.

4.2. Determination of free water in the putty

As a putty ages, the proportion of free water decreases and, conversely, the proportion of solids increases, because of the reaction $MgO + H_2O \rightarrow Mg(OH)_2$. At each test period the percentage of free water in the putty was determined, so that in the preparation of all test bars for autoclaving (described subsequently), a constant amount of hydrated lime on a dry-weight basis could be used.

The putty was first thoroughly remixed in the container to uniform consistency in order to redistribute any water that might have accumulated on the surface. About 2 to 4 g of putty was withdrawn on the tip of a spatula and spread thinly around the sides of a tared, 30-ml platinum crucible. This operation, together with the subsequent weighing of the crucible, was performed in the shortest possible time. The crucible was then heated for about 40 minutes in an oven maintained at 150° C, to drive off the free water. No attempt was made to dry the lime to constant weight as it was found that additional heatings usually resulted in slight increases in weight, which were ascribed to carbonation.

4.3. Determination of ignition loss of the dried putty

The ignition loss of the dried putty was obtained by heating the same sample used for the free-water determination to constant weight in an electric furnace maintained at about 1,020° C.

4.4. Preparation and testing of autoclave bars

The reader is referred to RP1917 [3] for a detailed procedure for preparing, curing, autoclaving, and measuring the expansion of test specimens made from dry hydrated lime. In the summary of that paper it was proposed that "hydrated limes be tested in the proportion of 1 cement : 1 lime (by weight), that the cement used have an expansion between 0.05 and 0.15 percent, that the autoclaving be done at 295-lb/in.^{2} gage pressure for 1 hr according to a controlled schedule . . . " No modification in procedure was necessary for the preparation and testing of bars made from dry hydrated lime and cement, designated "at start" in tables 2 and 3. However, for the preparation of bars made from wet aged lime putty some modification was necessary.

Following the free-water determination, described earlier, a quantity of putty sufficient to contain 150 g of dry solids was weighed into a 1-liter porcelain casserole. Next, 150 g of portland cement was added to the putty. These quantities were sufficient for the preparation of one test specimen.

For the remainder of the procedure, the operator wore rubber gloves. Immediately after addition of the cement, the mixture was squeezed and kneaded for 3 minutes. The mass was then allowed to stand undisturbed for 1 minute and finally vigorously reworked for 1 minute. At this point a Vicat penetration test for consistency was made according to the procedure given in Federal Specification SS–C–158b [10], paragraph F–47. It was found that the Vicat penetration decreased as the putty aged. In the earlier tests the penetration was greater than 10, but no attempt was made to remove water. In the later tests, whenever the putty had stiffened, water was added to the putty; then the whole mass was mixed to uniformity before the addition of cement. However, the adjustment of the consistency in these cases was only approximate.

Immediately after the determination of the Vicat penetration, the cement-lime putty was remixed for approximately 15 seconds. This putty then was molded into autoclave bar molds according to the procedure given in SS–C–158b, paragraph F–61. The bar molds provided for test specimens having a cross section of 1 in. by 1 in. and a 10-in. effective gage length, SS–C–158b, paragraph F–43.

Immediately after molding each specimen, the exposed surface was covered with a strip of waxed paper pressed down on the mold. This waxed paper minimized breakage during curing, caused by shrinkage cracks. The test specimens were stored in the molds in a moist closet for at least 20 hr, following the requirements of SS–C–158b, paragraph F–62.

At 23 ±1 hr after making the specimens, they were removed from the molds, measured for length, and placed in an electrically heated autoclave meeting the requirements of Federal Specification SS–C–158b [6] for an autoclave to be used in the testing of portland cement. The gage pressure of the autoclave was raised to 295 lb/in.^{2} within 1 to 1¼ hr, and maintained at 295 ±5 lb/in.^{2} for 1 hour. For most of the specimens, the reduction of the pressure and the subsequent cooling in water to 21° C were done as required in the procedure of autoclaving as given in Federal Specification SS–C–158b, paragraphs F–63e and F–63f, respectively. It was found necessary, however, to cool in air to 21° C those specimens that exhibited very high expansions (10% or more), because when cooled in water the greatly expanded specimens were apt to disintegrate.

For expansions under 2.5 percent, the comparator described in paragraph F–45 of SS–C–158b was used. For higher expansions, less exact methods, giving values to within a hundredth of an inch, were used.

5. Calculations

5.1. Percentage of magnesia hydrated at start

The method described in Proposed Amendment 1 to SS–L–351 [7] for calculating the percentage of hydrated MgO in a lime from the oxide analysis has been well established by Bureau researches [2, 3].

It is based essentially on the premise that CaO carbonates and hydrates before MgO. In the calculations, CO_2 is allotted to the molecular equivalent of CaO. The remaining CaO is allotted to an equivalent amount of H_2O. The amount of MgO hydrated is that equivalent to the remaining combined H_2O.

In the following derivation, I designates the ignition loss in percent and is equal to the sum of the CO_2 and the combined water. The formula for a compound represents also the percentage of that component present, as determined from the oxide analysis.

Combined water............ $=I-CO_2$
CaO equivalent to CO_2..... $=1.274\ CO_2$
CaO remaining............ $=CaO-1.274\ CO_2$
Combined H_2O equivalent to CaO remaining.[a] $=0.3213\ (CaO-1.274\ CO_2)$
Combined H_2O remaining.. $=(I-CO_2)-0.3213\ (CaO-1.274\ CO_2)$
Hydrated MgO (%), MgO_h,. $=2.238\ [(I-CO_2)-0.3213\ (CaO-1.274\ CO_2)]$ (1)
Unhydrated MgO......... $=$Total MgO$-$hydrated MgO (2)

5.2. Percentage of magnesia hydrated at time *t*

A formula for calculating the percentage of hydrated MgO in the solids portion of an aged putty can be derived from the oxide analysis of the original dry hydrated lime and the ignition loss of the dried putty at time *t*.

By substituting in the previously derived formula for MgO_h (eq 1) one can obtain an expression for the percentage of MgO hydrated at any time *t*,

$$\left.\begin{aligned}MgO_{h(t)}=2.238\ [(I_{(t)}-CO_{2(t)})\\ -0.3213\ (CaO_{(t)}-1.274\ CO_{2(t)})]\end{aligned}\right\}\quad(3)$$

where $MgO_{h(t)}$ represents the percentage of magnesia hydrated at time *t*, and the subscript (*t*) after I, CO_2, and CaO likewise refers to this time.

The oxide composition of a dried lime and its putty on an ignited basis is constant, however, regardless of aging. Thus the composition of a dried putty at time *t* can be expressed in terms of the analysis at the start (designated as *s*) and the ignition losses at times *s* and *t*.

For example,

$$\frac{CaO_{(s)}}{100-I_{(s)}}=\frac{CaO_{(t)}}{100-I_{(t)}}$$

$$CaO_{(t)}=CaO_{(s)}\left(\frac{100-I_{(t)}}{100-I_{(s)}}\right)\text{--------}(4)$$

A similar relationship holds for the other nonvolatile oxides. Assuming as negligible any additional carbonation of the lime putties during aging in the closed jars, the relationship given in eq 4 can be applied to the CO_2.

Making the appropriate substitution in eq 3

$$\left.\begin{aligned}MgO_{h(t)}=2.238\ \Bigg\{I_{(t)}-CO_{2(s)}\left(\frac{100-I_{(t)}}{100-I_{(s)}}\right)\\ -0.3213\left[CaO_{(s)}\left(\frac{100-I_{(t)}}{100-I_{(s)}}\right)\right.\\ \left.-1.274\ CO_{2(s)}\left(\frac{100-I_{(t)}}{100-I_{(s)}}\right)\right]\Bigg\}\end{aligned}\right\}\quad(5)$$

Combining terms and simplifying, the final equation is obtained

$$\left.\begin{aligned}MgO_{h(t)}=2.238I_{(t)}-(100-I_{(t)})\\ \frac{1.3220CO_{2(s)}+0.7191CaO_{(s)}}{100-I_{(s)}}\end{aligned}\right\}\quad(6)$$

---

[a] If the calculated value is larger than that of the combined water, unhydrated CaO is present.

When the values at the start s are substituted in eq 6, it reduces to the following linear form

$$\mathrm{MgO}_{\mathrm{h}(t)}=AI_{(t)}-B, \tag{7}$$

where A and B are constants for a particular lime.

5.3. Other equations

Several other equations can be derived for calculating the percentage of magnesia hydrated at time t, $\mathrm{MgO}_{\mathrm{h}(t)}$, by the application of simple algebraic principles.

One such equation, involving only the magnesia hydrated at the start, $\mathrm{MgO}_{\mathrm{h}(s)}$, and the ignition losses, is

$$\left.\begin{aligned}\mathrm{MgO}_{\mathrm{h}(t)}=&\frac{I_{(t)}(223.8-\mathrm{MgO}_{\mathrm{h}(s)})}{100-I_{(s)}}\\&+\frac{100\,\mathrm{MgO}_{\mathrm{h}(s)}-223.8\,I_{(s)}}{100-I_{(s)}}\end{aligned}\right\} \tag{8}$$

5.4. Sample data sheet

A typical data sheet (for lime 34) is given in table 2, showing simplification of the formulas,

Table 2. *Typical data sheet, including chemical analysis and simplified formulas*

Lime 34. Chemical analysis (after drying at 150° C)

	Percent
Ignition loss	18. 41
CO_2	1. 76
CaO	47. 41
MgO	33. 48
SiO_2	0. 40
R_2O_3	. 28
Total	99. 98
Hydrated MgO, $\mathrm{MgO}_{\mathrm{h}(s)}$,	4. 79
Unhydrated MgO, $\mathrm{MgO}_{\mathrm{u}(s)}$,	28. 69
Percentage of total MgO hydrated, $\frac{\mathrm{MgO}_{\mathrm{h}(s)}}{\mathrm{MgO}_{(s)}}\times 100$,	14. 31

Equations

Total MgO at time t:[1]

$$\mathrm{MgO}_{(t)}=\mathrm{MgO}_{(s)}\left(\frac{100-I_{(t)}}{100-I_{(s)}}\right)=33.48\left(\frac{100-I_{(t)}}{100-18.41}\right)=0.41034(100-I_{(t)}) \tag{a}$$

MgO hydrated at time t:[2]

$$\begin{aligned}\mathrm{MgO}_{\mathrm{h}(t)}&=2.238I_{(t)}-(100-I_{(t)})\frac{(1.3220\mathrm{CO}_{2(s)}-0.7191\mathrm{CaO}_{(s)})}{100-I_{(s)}}\\&=2.238I_{(t)}-(100-I_{(t)})\frac{(1.3220\times 1.76-0.7191\times 47.41)}{(100-18.41)}\\&=2.6844I_{(t)}-44.637\end{aligned} \tag{b}$$

Calculated ignition loss
at 100% hydration: I (100%)=27.68% [obtained by equating (a) to (b)] ---------- (c)

Tabulation

	Time (weeks)								
	At start	1/7	3/7	1	2	4	8	12	16
	Percent	*Percent*	*Percent*	*Percent*	*Percent*	*Percent*	*Percent*	*Percent*	*Percent*
$I_{(t)}$	--------	19. 41	20. 74	22. 51	24. 20	25. 88	27. 20	27. 42	27. 62
$100-I_{(t)}$	--------	80. 59	79. 26	77. 49	75. 80	74. 12	72. 80	72. 58	72. 38
$\mathrm{MgO}_{(t)}$	33. 48	33. 07	32. 52	31. 80	31. 10	30. 41	29. 78	29. 78	29. 70
$\mathrm{MgO}_{\mathrm{h}(t)}$	4. 79	7. 47	11. 04	15. 80	20. 33	24. 84	28. 38	28. 98	29. 51
Unhydrated $\mathrm{MgO}_{(t)}$	28. 69	25. 60	21. 48	16. 00	10. 77	5. 57	1. 49	0. 80	0. 19
$\frac{\mathrm{MgO}_{\mathrm{h}(t)}}{\mathrm{MgO}_{(t)}}$	14. 31	22. 59	33. 95	49. 67	65. 37	81. 68	95. 01	97. 31	99. 36
Expansion	9. 2	9. 0	9. 0	6. 8	6. 1	2. 7	0. 37	0. 32	0. 21

---

[1] Equation (a) is a variant of eq 4, p. 4.
[2] Equation (b) is eq 6, p. 4.

after substitution of the constants and the values determined. The chemical analysis for this lime, as given in table 1, columns 3 to 11, inclusive, and the ignition losses, columns 12 to 20, inclusive, are repeated for the purpose of convenience.

The calculated ignition loss at 100-percent hydration was obtained for this lime by equating the simplified expression for the MgO hydrated at time t (eq b) to that for the total MgO present at time t (eq a) and solving for $I_{(t)}$ (eq c). This value was of practical importance, since by comparing it with the experimentally determined ignition loss at a given time, one could rapidly note the approach of the sample to complete hydration. At complete hydration, the value also served as an approximate check on the accuracy of the chemical analysis and the calculations, as it was the theoretical maximum ignition loss that could be obtained.

6. Results and discussion

Table 1 gives the chemical analysis and the calculated percentages of hydrated magnesia and unhydrated oxides for the 18 regularly hydrated dolomitic limes, together with the ignition losses (after drying) of aged putties made from these limes. From these data, the percentage of total magnesia hydrated in each putty at the various testing periods was calculated, as shown in the typical data sheet (table 2). The results are recorded in table 3, together with the corresponding linear autoclave expansion of cement-lime putty bars (proportioned 1 to 1 on dry weight basis). It may be noted that all values obtained from chemical analyses are reported to the nearest 0.01 percent. The calculated hydrated magnesia, unhydrated oxides, and proportion of magnesia hydrated for all limes and putties also have been reported to the nearest 0.01 percent. However, it should be emphasized that the accuracy of these calculated values is not known to 0.01 percent. The reproducibility of determining percentage of expansion of cement-lime test specimens is discussed in RP1917 [3].

Figures 1 and 2 show the effect of time of aging on the percentage of total magnesia hydrated and on the linear expansion of cement-lime putty bars (1:1, by dry weight) for the 18 regularly hydrated dolomitic limes. The limes are arranged according to increasing time required for the expansion of the cement-lime putty bar to decrease to 1 percent. One percent was chosen as the basis for comparison because it is the suggested limit of expansion proposed in a test for determining the soundness of hydrated limes, described in Bureau Research Paper RP1917 [3].

Several conclusions are at once apparent from these figures. Most striking is the correlation

TABLE 3. *Percentages of total magnesia hydrated in 18 regularly hydrated dolomitic limes and in aged putties made from these limes, together with the autoclave expansions of cement-lime bars made from the hydrates and putties*

Lime	Calculated proportion of total magnesia hydrated (time in weeks)											Linear expansion of cement-lime putty bar (proportioned 1 to 1 on dry-weight basis) (time in weeks)										
	At start [a]	¼	¾	1	2	4	8	12	16	20	32	At start [b]	¼	¾	1	2	4	8	12	16	20	32
	%	%	%	%	%	%	%	%	%	%	%	%	%	%	%	%	%	%	%	%	%	%
23	31.55	34.10	40.45	45.61	51.89	61.51	75.48	83.71	89.33	95.14	95.55	15.2	12.1	11.7	12.0	12.5	9.1	6.5	4.3	3.6	2.6	2.2
24	13.50	18.39	21.13	31.86	45.50	66.83	86.69	92.80	96.66	------	------	8.5	8.2	7.4	7.0	5.6	2.6	0.56	0.28	0.22	------	-----
27	26.96	35.25	42.98	54.36	67.53	81.21	93.34	99.09	98.56	------	------	9.4	7.3	7.0	6.9	4.0	2.6	.46	.17	.18	------	-----
28	25.76	25.68	31.64	44.23	55.70	68.71	81.50	86.93	89.60	90.52	------	12.1	12.8	11.9	10.6	9.0	7.2	3.7	1.5	.87	0.71	-----
29	27.26	34.59	42.35	52.76	62.43	74.61	86.63	90.14	92.66	93.41	------	8.8	8.3	7.0	6.0	4.9	3.0	0.59	0.36	.27	.22	-----
30	24.49	32.88	42.88	53.27	63.67	77.06	90.03	93.21	95.54	96.25	------	7.5	7.4	6.6	6.8	4.7	2.6	0.46	0.27	0.22	0.18	-----
31	21.59	27.37	32.24	44.41	59.23	77.43	91.68	95.53	97.49	------	------	10.7	11.2	9.5	8.6	6.6	3.6	.60	.31	0.24	------	-----
34	14.31	22.59	33.95	49.67	65.37	81.68	95.01	97.31	99.36	------	------	9.2	9.0	9.0	6.8	6.1	2.7	.37	.32	.21	------	-----
35	18.14	25.19	27.74	37.40	47.59	59.19	74.90	82.48	86.12	87.34	91.22	14.9	15.5	15.5	14.7	13.6	11.8	8.1	5.5	4.6	4.0	2.3
37	25.23	32.58	46.82	60.26	74.56	87.67	96.43	97.65	100.20	------	------	6.7	6.2	5.3	1.8	1.7	0.89	0.26	0.27	0.17	------	-----
38	9.76	12.58	19.88	28.29	36.29	48.22	66.49	78.79	84.15	86.66	91.84	17.7	16.8	71.2	17.2	15.2	14.4	9.1	4.8	2.8	1.8	0.66
40	13.74	15.84	26.89	39.10	55.21	75.63	92.02	95.23	98.20	97.48	------	12.6	(c)	11.8	10.7	8.6	4.9	0.88	0.35	0.27	0.22	-----
43	10.88	15.97	22.87	39.19	60.29	82.84	98.73	100.08	102.58	------	------	11.4	10.9	(c)	8.5	6.2	2.9	.27	.19	.17	------	-----
44	14.62	22.25	24.51	34.76	44.22	63.55	84.04	92.00	96.40	97.98	------	14.3	13.1	13.1	12.3	9.4	5.9	3.4	1.5	.78	.41	-----
45	10.85	19.96	31.58	56.21	76.96	91.33	98.07	98.63	100.00	------	------	9.8	8.0	7.5	5.0	2.8	0.72	0.17	0.13	.13	------	-----
46	6.42	13.76	17.09	28.17	40.58	60.27	82.18	90.71	94.47	96.48	------	17.3	16.6	17.0	17.4	15.2	11.6	5.1	2.4	1.1	0.61	-----
47	7.21	10.99	15.87	28.05	47.53	70.16	90.12	96.43	96.83	97.14	------	13.2	10.5	9.2	8.7	6.7	4.5	0.91	0.51	0.31	0.29	-----
48	0.00	5.26	4.19	12.12	29.20	60.92	86.34	92.03	94.81	95.84	96.50	16.0	13.9	14.1	13.5	11.3	7.6	4.0	2.4	1.9	1.6	1.2
Avg, $\Sigma d/n$	16.8	22.5	29.2	41.1	54.7	71.6	87.2	92.4	95.2	[d] 96.1	------	12.0	11.0	10.6	9.7	8.0	5.5	2.5	1.4	1.0	[d] 0.8	-----

[a] Dried hydrated lime as received; value derived from columns 8 and 10, table 1.

[b] Bar made with hydrated lime as received.

[c] Bar cracked during curing.

[d] Average based on all 18 samples, using extrapolated values where no figures are given.

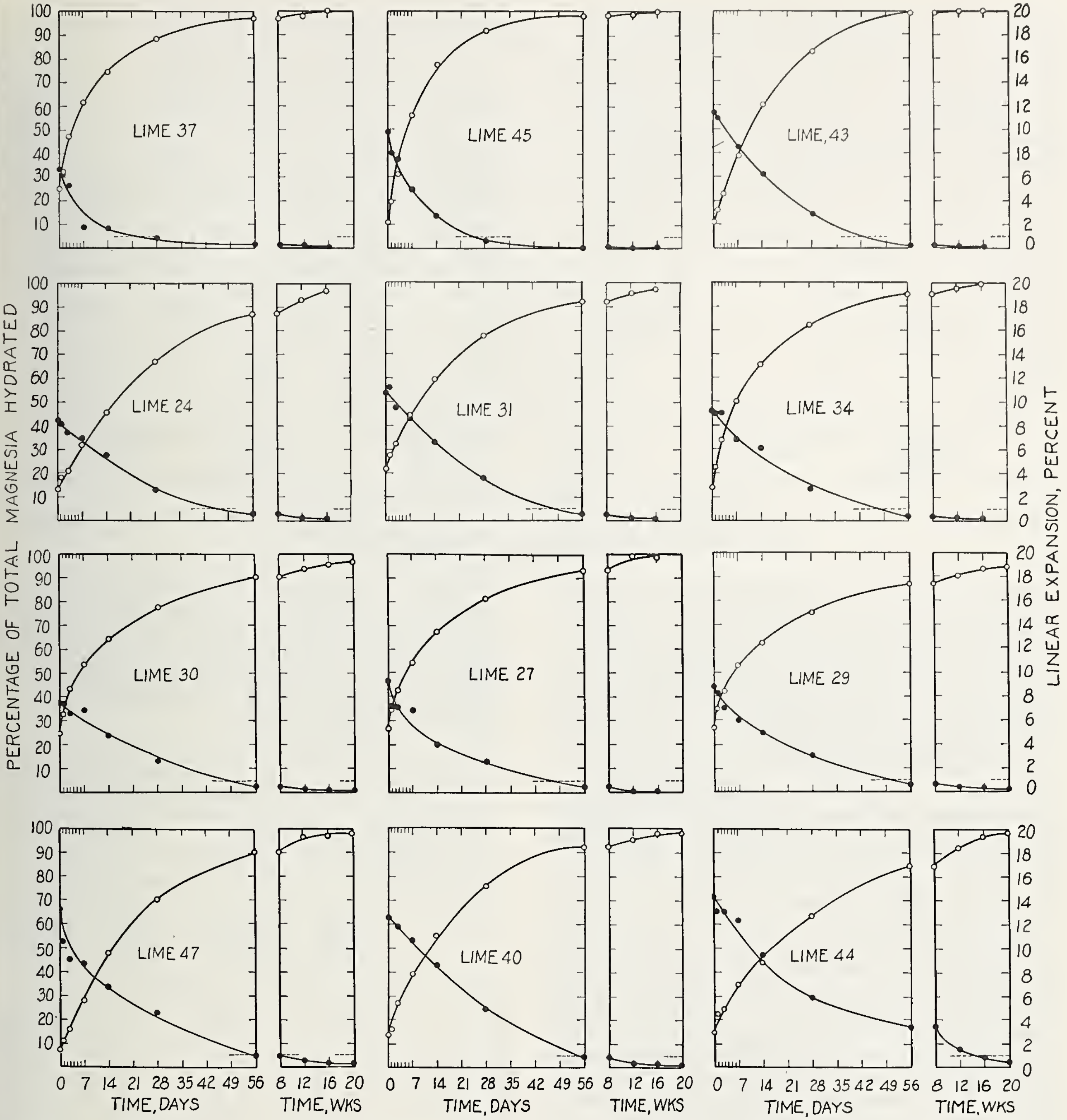

FIGURE 1. *Effect of time of aging lime putties at 21° C (70° F) on the increase in magnesia hydrated and on the decrease in autoclave linear expansion of cement-lime putty bars.*

The twelve regularly hydrated limes used are arranged according to increasing time required for expansions of cement-lime putty bars (1:1 by dry weight) to be reduced to one percent when autoclaved for 1 hour at a gage pressure of 295 lb/in².

○, Magnesia hydrated. ●, Linear expansion (autoclave).

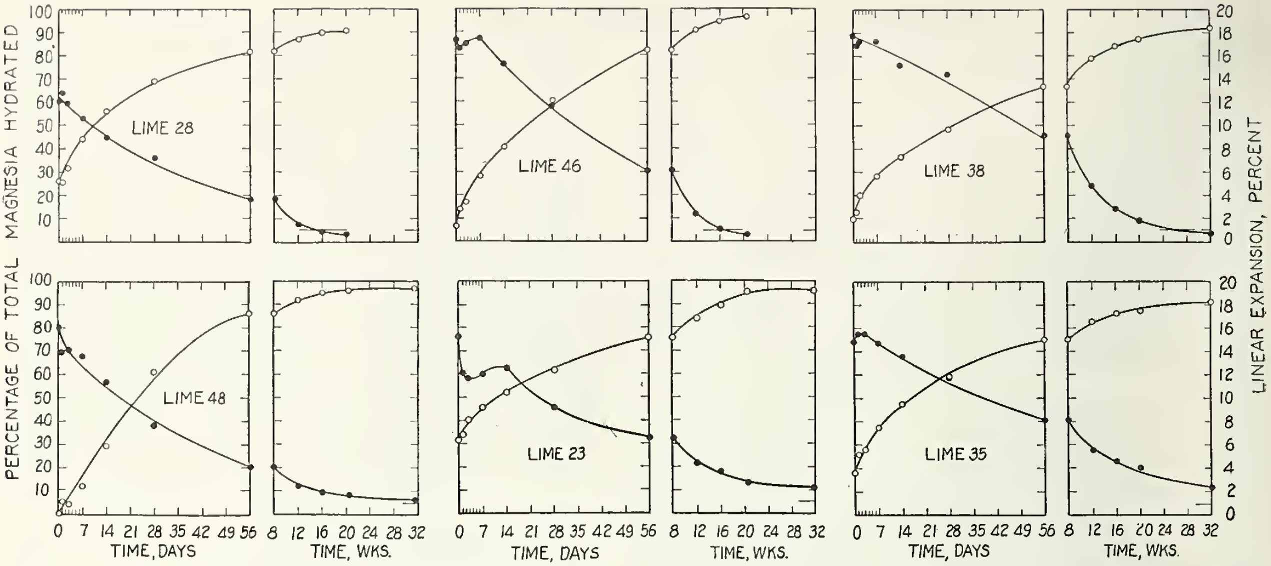

Figure 2. *Effect of time of aging lime putties at 21° C (70° F) on the increase in magnesia hydrated and on the decrease in autoclave linear expansion of cement-lime putty bars.*

The six regularly hydrated limes used are arranged according to increasing time required for expansions of cement-lime putty bars (1:1 by dry weight) to be reduced to one percent when autoclaved for 1 hour at a gage pressure of 295 lb/in^2.
○, Magnesia hydrated. ●, Linear expansion (autoclave).

between percentage of magnesia hydrated in lime putty during aging and autoclave expansion of cement-lime bars made from the putty. For any one lime, as the percentage of magnesia hydrated increases, the percentage of linear expansion decreases; thus, as the hydration of the magnesia approaches 100 percent, the linear expansion approaches 0.2 to 0.3 percent.

In comparing the behavior of different limes with respect to the effect of aging on hydration characteristics of the putties and on expansion, it appears that a slow rate of hydration is attended by a slow decrease in expansion. The effect is particularly apparent by comparing extreme differences, as shown in figures 1 and 2, for example, lime 37 with lime 35.

Table 4 gives the times of aging of lime putties at which the expansions of cement-lime putty bars were 1 percent; the corresponding percentages of total MgO hydrated in the putties; the expansions of cement-lime bars prepared from the dry hydrated limes (as received); and the corresponding percentages of unhydrated oxide in the dry lime. These expansion and hydration values at the 1-percent point for the different limes were obtained from figures 1 and 2.

It can be seen that the shortest time of aging required to reduce the expansion to 1 percent was 3 weeks (lime 37); the next shortest time was 4 weeks (lime 45), followed by nine others, or half the total number, distributed over a period of 6 to 8 weeks. The remaining seven limes required much longer periods, and three (48, 23, and 35) gave expansions in excess of 1 percent, even after 32 weeks of aging.

It is also apparent from table 4 that at least 83 percent of the total MgO was hydrated before the expansion was reduced to 1 percent; and in two cases over 97-percent hydration was required. The figures and table 4 reveal the fact that the limes differed markedly from one another, both in regard to the time required to reach a given percentage of expansion and to the extent of hydration at the given expansion.

Table 4.—*Times of aging of lime putties required to reduce the autoclave linear expansions of cement-lime putty bars to 1 percent and the corresponding percentages of total* MgO *hydrated in the putties, together with the expansions of cement-lime bars prepared from the dry hydrated limes "as received" and the corresponding percentages of unhydrated* MgO *in the dry lime*

Lime	Time required to reach 1 percent expansion	MgO hydrated at 1 percent expansion	Expansion of bar made with dry hydrated lime "as received" [a]	Unhydrated MgO in dry hydrated lime "as received" [b]
	Weeks	*Percent*	*Percent*	*Percent*
37	3	83	6.7	24.98
45	4	92	9.8	31.33
43	6	95	11.4	30.30
24	6.5	83	8.5	22.43
31	7	91	10.7	26.12
34	7	93	9.2	28.69
30	7	88	7.5	24.32
27	7	91	9.4	24.06
29	7	85	8.8	23.06
47	8	90	13.2	31.27
40	8	92	12.6	29.26
44	14	94	14.3	28.45
28	16	90	12.1	24.26
46	16	95	17.3	32.05
38	26	91	17.7	29.76
48	Over 32 [c]	Over 97	16.0	33.59
23	Over 32 [d]	Over 96	15.2	21.80
35	Over 32 [e]	Over 91	14.9	26.85

[a] From table 3, column 13.
[b] From table 1, column 11.
[c] 1.2-percent expansion at 32 weeks.
[d] 2.2-percent expansion at 32 weeks.
[e] 2.3-percent expansion at 32 weeks.

A factor of prime importance in explaining the variability exhibited by the different limes is the reactivity of the constituent MgO. The reactivity of the MgO is closely connected with the phenomenon of overburning in the lime kiln during the conversion of the limestone to quicklime. The extent of overburning with the resultant decrease in reactivity of the oxides to water is increased with temperature as well as with the time of burning. As $MgCO_3$ decomposes at a much lower temperature than $CaCO_3$ and as MgO is susceptible to overburning, it follows that dolomitic quicklimes contain overburned MgO the reactivity of which varies greatly depending on the conditions of burning.[3] Variation in the reactivity of the MgO is manifested by (1) the extent to which MgO is converted to $Mg(OH)_2$ in the production of the hydrate from the quicklime (table 3, column 2); (2) the rates of hydration of the MgO when the lime is hydrated further as a putty (table 3 and figs. 1, 2); and (3) the different values of autoclave expansions of cement-lime bars attending the hydration, within the autoclave, of equal quantities of MgO.

The third case is clearly evident in figure 3, where the percentages of unhydrated oxide in all the limes and putties at each test period are plotted against the corresponding percentages of linear expansion of the autoclaved cement-lime putty bars. The percentage of unhydrated oxide for each lime at a given period was calculated from the data in table 1, according to the method illustrated in table 2. From figure 3 it can be seen that although there is a strong trend for increased unhydrated oxide to be associated with increased expansion, nevertheless, the points are spread fan-shaped from the origin and that, in general, the expansions vary for a given percentage of unhydrated oxide.

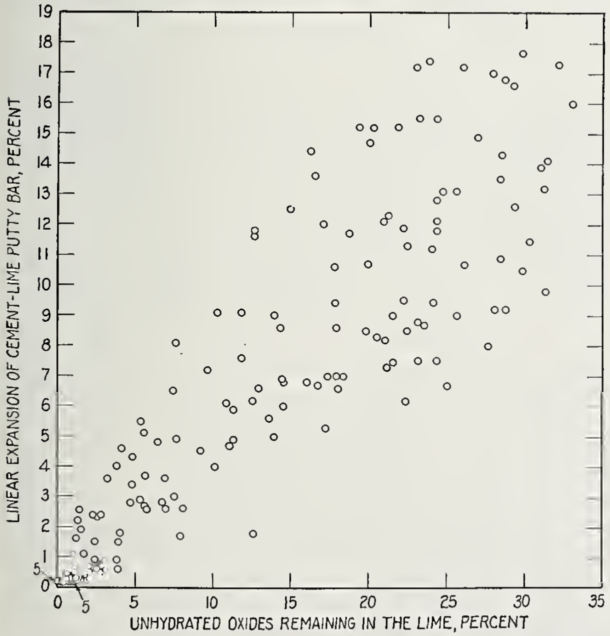

Figure 3. *Relation between percentage autoclave linear expansion of cement-lime putty bars (1:1 by dry weight) and unhydrated oxide* (MgO) *in putties at the various test periods.*

The same conclusions are reached from figure 4, which has been reproduced from a previous publication [3, fig. 8]. Figures 3 and 4 are comparable, but it is interesting to note that in figure 4, variations in unhydrated oxide were obtained essentially by using many limes of different types rather than by aging putties of a selected few regularly hydrated dolomitic limes, as for figure 3. By testing high-calcium, magnesian, highly hydrated dolomitic, and regularly hydrated dolomitic limes, it was possible to cover the range of unhydrated oxide from 0 to 34 percent, in figure 4.

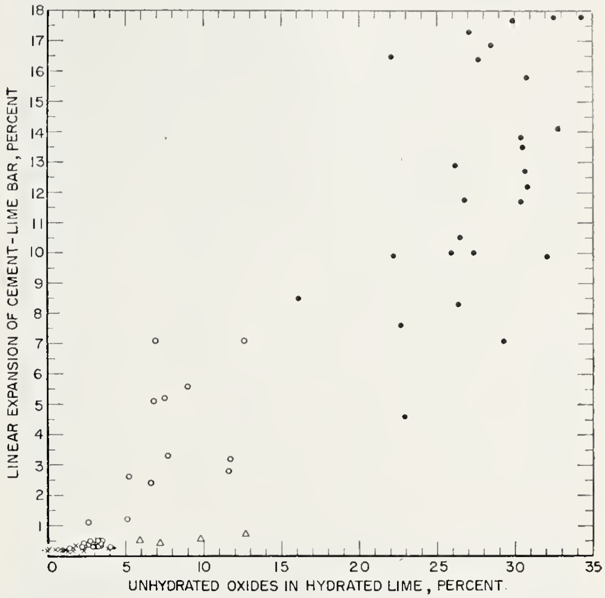

Figure 4. *Linear expansion of cement-lime bars prepared with hydrated limes containing various amounts of unhydrated oxides, in the proportion of 1 cement to 1 lime (by weight) and subsequently autoclaved for 3 hours at a gage pressure of 295 lb/in².*

See figure 8 of RP1917 [3].

The specimens were prepared with a cement, which, without addition of hydrated lime, had a linear autoclave expansion of 0.11 percent.

×, High-calcium; ●, regularly hydrated dolomitic; ○, highly hydrated dolomitic; △, magnesian.

A careful comparison of figures 3 and 4 reveals an apparent discrepancy between the two. It can be seen that the spread of expansion values associated with unhydrated oxide of under 5 percent is different in the two figures. In figure 4, all but one of the limes (actually 37 out of 38) show expansions of less than 1 percent when the unhydrated oxide is under 5 percent, whereas in figure 3, only about two-thirds of the expansion values (actually 44 out of 63) are less than 1 percent for the same range of unhydrated oxide. However, the distribution of the 19 exceptions is not apparent from figure 3. Actually, all of the exceptions occurred among the seven limes requiring aging periods of 14 weeks or longer before expansions were reduced to 1 percent (table 4, limes 44, 28, 46, 38, 48, 23, 35); furthermore, 12 of the exceptions occurred among the 3 limes requiring more than 32 weeks (table 4, limes 48, 23, 35).

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[3] A more complete discussion of overburning is given in BMS121 [1].

It is a significant fact that the lime putties requiring the longest aging periods to effect a reduction in expansion to 1 percent yield the highest expansions for a given percentage of unhydrated MgO. This again may be explained by the process of overburning. It should be borne in mind that in the commercial production of lime the degree to which the MgO is overburned is not likely to be uniform for the whole mass of MgO, because in the calcining process the dolomite is added in lumps and consequently a temperature gradient exists between the surface of the lump and the core. However, the bulk of the MgO is sufficiently overburned so that little is hydrated in the normal process of producing a hydrated lime. During the aging of a lime as a putty, apparently the less overburned MgO, being more reactive, hydrates first, leaving behind the more overburned, less reactive, MgO. However, regardless of the state of overburning, all of the MgO hydrates under the temperature conditions of the autoclave test. But the highly overburned MgO gives rise to the largest expansions in the autoclave.

Preliminary experiments with cement-MgO bars prepared with MgO of different reactivity have verified the conclusion that it is the less reactive MgO which gives rise to the greater expansions in the autoclave. The MgO was prepared by completely hydrating reagent quality MgO in an autoclave at 295 lb/in.^{2} and subsequently heating portions of the $Mg(OH)_2$ at 500°, 1,000°, and 1,300° C. The corresponding percentages of expansion of the cement-MgO bars, containing in each case 5 percent of MgO, were 0.12, 0.27, and 5.0. The expansion of the neat cement bar was 0.11 percent.

Table 4 reveals the interesting fact that the group of 7 limes whose putties required aging periods of 14 weeks or longer to effect a reduction in expansion to 1 percent had the greatest autoclave expansions when tested on the "as received" basis. The average expansion value at the start for these seven limes was 15.4 percent as compared to an average of 9.8 percent for the other 11 limes. However, the average value for the unhydrated oxide of the seven limes was 28.1 percent as compared to an average of 26.9 percent for the remaining limes. The small average difference of 1.2 in the percentage of unhydrated oxide in the two groups is not statistically significant and does not adequately account for the large difference in autoclave expansion of 5.6 percent.

It may be added that the seven limes whose putties required aging periods of 14 weeks or longer to effect a reduction in autoclave expansion to 1 percent when tested in the proportion of 1 cement to 1 lime had the greatest expansions when tested on the "as received" basis not only for that proportion but also for the 2 cement to 1 lime and 1 cement to 2 lime proportions.[4]

Thus there is added evidence that the degree of overburning is of prime importance and that the autoclave expansion of a bar is the resultant effect of two fundamental factors: (1) the total quantity of unhydrated MgO present; and (2) the reactivity of the MgO, which is a measure of the degree to which the lime has been overburned during the calcining process, which, in turn, is a function of stone size and time and temperature of calcining. It is obvious that the autoclave test in addition to serving as a soundness criterion for hydrated lime also shows promise as a possible control method for determining the degree of overburning.

It is known that increasing the temperature and/or time of calcining increases the degree of overburning of a lime. Also, as the degree of overburning increases the, bulk densities of the CaO and MgO increase, indicating a consolidation of the molecules and a reduction in surface area. Staley and Greenfeld [11], in a study of the surface areas of high-calcium quicklimes by the nitrogen adsorption method, have found that the surface area of CaO decreases appreciably both with increased temperature and time of burning. More recently, Murray, Fischer, and Sabean [12], in a study of the effect of time and temperature of burning on the properties of quickline prepared from calcite, have shown that the porosity, surface area, and activity of the quicklime are closely related, and that high values of porosity are associated with high values of surface area and with high values of activity with water.

The surface area of MgO should be decreased even more than in the case of CaO, because MgO is more susceptible to overburning than CaO. Inasmuch as about one-quarter to one-third of regularly hydrated dolomitic lime consists of overburned MgO, extent of overburning may be reflected in the surface area.

Consequently, surface areas of the 18 hydrated limes were determined by the nitrogen adsorption method. Samples were sealed in glass adsorption cells and evacuated at 100° C overnight to a pressure of approximately 1×10^{-6} mm of Hg. The quantity of space of each sample holder not occupied by the solid adsorbent was determined with helium. Adsorption tests were made using purified nitrogen gas with samples in a bath of liquid nitrogen. The quantities of nitrogen adsorbed were determined at four to six partial pressures in the range of 0.05 to 0.30 mm of Hg for each sample. Surface areas of all samples were evaluated by means of the Brunauer-Emmett-Teller equation [13], assuming that the nitrogen molecule occupies an area of 16.2 square angstroms.

Table 5 gives the results of the determinations of surface areas expressed as square meters per gram. For convenience of comparison, the linear expansion of cement-lime bars prepared from the dry hydrated limes (as received), and the corresponding percentage of unhydrated MgO in the dry lime are also included. The limes are arranged in the order of increasing expansion. Inspection of the table indicates a tendency of the surface areas to decrease with an increase in the autoclave expansions of the hydrated limes "as received."

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[4] The autoclave expansion values for the bars proportioned 2 cement to 1 lime and 1 cement to 2 lime are given in table 1 and figures 7, 9, and 10 of RP1917 [3].

Table 5. *Surface areas available to nitrogen for 18 regularly hydrated dolomitic limes arranged in order of increasing autoclave linear expansions of cement-lime bars prepared from the dry hydrated limes "as received", and the corresponding percentages of unhydrated MgO in the dry lime*

Lime	Expansion of bar made with dry hydrated lime "as received"[a]	Unhydrated MgO in dry hydrated lime "as received"[b]	Surface area available to nitrogen
	Percent	*Percent*	*m²/g*
37	6.7	24.98	12.9
30	7.5	24.32	12.7
24	8.5	22.43	10.0
29	8.8	23.06	12.6
34	9.2	28.69	11.8
27	9.4	24.06	12.7
45	9.8	31.33	11.0
31	10.7	26.12	11.6
43	11.4	30.30	11.3
28	12.1	24.26	11.7
40	12.6	29.26	8.2
47	13.2	31.29	9.1
44	14.3	28.45	12.8
35	14.9	26.85	9.9
23	15.2	21.80	10.5
48	16.0	33.59	7.5
46	17.3	32.05	9.4
38	17.7	29.76	8.0

[a] From table 3, column 13. [b] From table 1, column 11.

Figure 5 is a scatter diagram of the linear expansion and surface area. The line fitting these data, determined by the method of least squares, is

$Y=26.3-1.33\,X$, where Y is the value of the linear expansion and X the value of the surface area. The coefficient of correlation between the linear expansion and surface area is

$r=-0.7$, where $r=\Sigma XY/\sqrt{\Sigma X^2 \Sigma Y^2}$

Hence, there is a significant correlation between the linear expansion of cement-lime bars prepared from regularly hydrated dolomitic limes and the surface area of these hydrates.

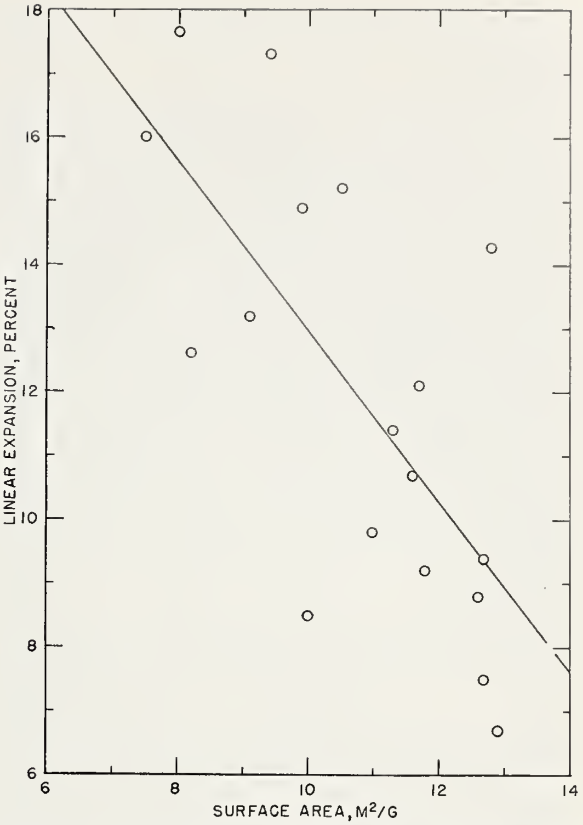

Figure 5. *Relation between autoclave linear expansion of cement-lime bars in the proportion of 1 cement to 1 lime (by weight), table 3, column 13, and surface area of 18 regularly hydrated dolomitic limes*

In considering these data it should be mentioned that the samples were obtained from several widely separated lime-producing centers. Dolomitic limestone differs from one area to another, and the characteristics of a quicklime are related to the limestone from which it is made. Likewise, the properties of a hydrated lime, such as fineness and plasticity, are largely determined by those of the quicklime. It should be emphasized that about two-thirds to three-quarters, by weight, of regularly hydrated dolomitic lime, is composed of materials other than MgO, primarily $Ca(OH)_2$ and smaller amounts of $Mg(OH)_2$. The presence of these hydrates tends to mask differences in surface area attributed to the MgO. All of these factors contribute to the scattering of the points in figure 5. In addition, the quantity of unhydrated MgO is not a constant. These factors also tend to mask differences in surface areas of MgO resulting from differences in degree of overburning.

Nevertheless, in spite of these variables, the extent of overburning of MgO during the calcining process, as reflected by increased autoclave expansions of cement-lime bars, is also manifested in lower surface areas of the partially hydrated limes.

The relation, however, needs further study. An investigation should be undertaken of the effect of overburning on the autoclave expansion, using hydrates obtained from quicklimes produced from dolomitic limestone from a single source and burned and hydrated under carefully controlled conditions.

Consideration will now be given to a slight error involved in the rapid method used for determining the quantity of unhydrated MgO in the putties. The error arose from the procedure for expelling the free water from the putties, by drying in an oven maintained at 150° C. Unquestionably, hydration of some additional MgO occurred during the brief drying period. An estimate of the extent of this hydration was ascertained by a simple experiment.

Putties were made from three of the dry hydrates, and after a 15-minute aging period, they were dried and ignited according to the rapid method described previously. Calculated from these data, the unhydrated oxide content of the lime portion of the putty was compared with the value determined for the dry hydrated lime and based solely on the oxide analysis. The assumptions were made that no additional hydration had occurred during the 15-minute soaking period and that the only difference between the two methods was reflected in the additional hydration occurring during drying in the rapid method. Values for the unhydrated oxide content obtained by the rapid method were from 1 to 4 percent higher than those calculated for the dry lime, and a trend was indicated for the greatest differences to be associated with the limes whose putties hydrated most rapidly.

It should be emphasized that in determining the percentage of unhydrated oxide in the putty by the rapid method, the error is greatest in the early stages of aging when the MgO still contains the most reactive fractions. As aging proceeds, however, selective hydration occurs; and as the more reactive fractions hydrate, the error should decrease. Consequently, it is believed that the high expansion values obtained in some cases with putties containing a surprisingly low percentage of unhydrated oxide are essentially correct.

Figure 6 shows the effect of time of aging on the percentage of magnesia hydrated for all of the lime putties, plotted on one set of coordinates. For the purpose of clarity, values for the percentage of magnesia hydrated in the dry lime, "as received," are omitted. A heavy black line is drawn through the arithmetical average for each test period, as given in table 3.

The wide variation in percentages of magnesia hydrated at each test period is evident from the spread of values. The average values of magnesia hydrated at the start, and at 1, 3, and 7 days are 16.8, 22.5, 29.2, and 41.1 percent, respectively (see also table 3). These figures are in agreement with those reported in 1937 by Wells and Taylor [2] for six regularly hydrated dolomitic lime putties at corresponding ages, namely, 12.5, 19.1, 30.2, and 40.9 percent, respectively. Thus it is evident that the regularly hydrated dolomitic lime of the present time is fundamentally the same as that produced in 1937. In fact, calculations based on the analyses of 185 regularly hydrated dolomitic limes submitted to the Bureau for test for compliance with Federal Specification SS–L–351 [5] from 1923 to 1940 show that the average percentage of total magnesia hydrated was 17.0 [1].

Figure 7 shows the effect of time of aging on the percentage of linear expansion of cement-lime putty bars (1:1 by dry weight) for all of the lime putties, plotted on one set of coordinates. As in figure 6, values for the dry hydrated lime "as received" have not been included, and a heavy black line has been drawn through the arithmetical averages (values given in table 3).

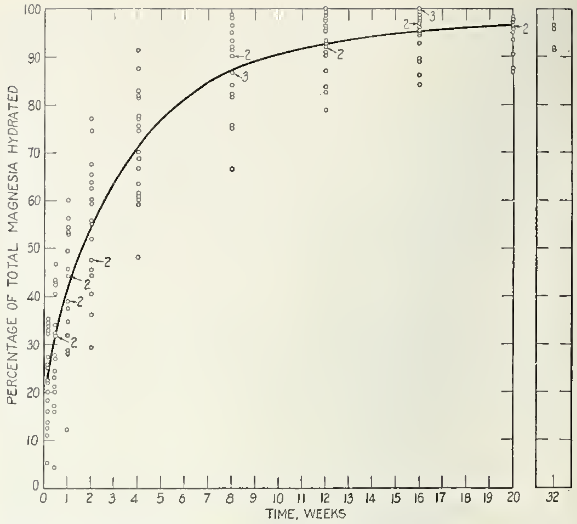

FIGURE 6. *Effect of time aging on the percentage of total magnesia hydrated for all of the putties prepared from the 18 regularly hydrated dolomitic limes.*

The heavy black line is drawn through the arithmetical average for each test period, as given in table 3.

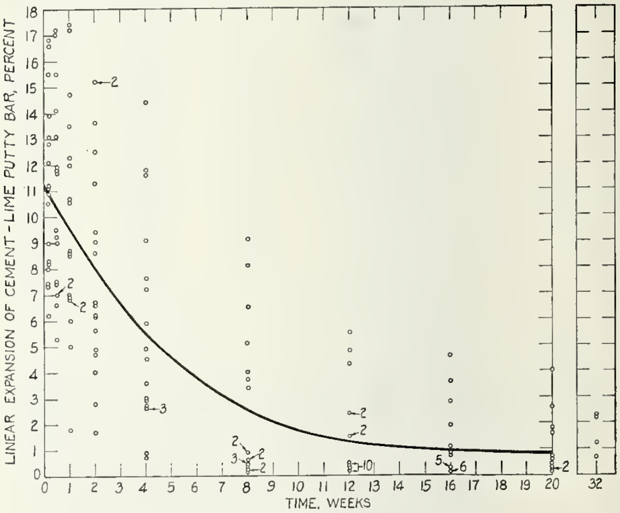

FIGURE 7. *Effect of time of aging on the percentage of autoclave linear expansion of cement-lime putty bars (1:1 by dry weight) for all of the lime putties prepared from the 18 regularly hydrated dolomitic limes.*

The heavy black line is drawn through the arithmetical average for each test period, as given in table 3.

The wide variation in percentages of expansion at each test period is evident. The average linear expansion at the start, 1, 3, and 7 days is 12.0, 11.0, 10.6, and 9.7 percent, respectively (see table 3). At 16 weeks the average expansion is 1 percent, with 13 of the 18 limes under the 1-percent value. The average amount of magnesia hydrated at this time is 95.2 percent (table 3). It can be clearly seen by comparing figure 5 with 6, that as the percentage of magnesia hydrated in the putties increases, the percentage of linear expansion of the bars decreases.

7. Summary and Conclusions

The progressive hydration of magnesia in dolomitic lime putties upon aging and the attendant decrease in expansion of cement-lime putty bars were studied.

Eighteen regularly hydrated dolomitic limes (also designated as type N—normal finishing hydrated limes) representative of commercial production were made into putties; and these were stored in airtight containers and aged in a constant-temperature room maintained at 21° ±1°C (70° ±2°F).

At progressive time periods (in weeks) of 1/7, 3/7, 1, 2, 4, 8, 12, 16, 20, and 32, representative samples of the putties were removed, and determinations were made for free water and ignition loss. From these determinations and the chemical analysis of each dry hydrated lime, as received, the percentages of total magnesia hydrated in the lime of the putties were calculated. A portion of each lime putty was then mixed with portland cement in the proportion of 1:1 on a dry-weight basis and cast into bars. Subsequently, the linear expansions were ascertained after autoclaving the bars at 295 lb/in.^{2} for 1 hr.

Equations were derived for calculating the percentage of unhydrated oxide and the percentage of total magnesia hydrated in a dry lime and in an aged putty.

For any particular lime, as the percentage of magnesia hydrated in the putty increased, the percentage of autoclave expansion of the corresponding cement-lime putty bar decreased; but neither the rate of increase of hydration nor the rate of decrease of expansion was a linear function of time. As the amount of magnesia hydrated approached 100 percent, the autoclave expansion approached 0.2 to 0.3 percent.

The limes differed markedly both in regard to the time required to reach a given percentage of expansion and to the extent of hydration at the given expansion. The shortest time of aging required to reduce the expansion to 1 percent (a suggested specification limit) was 3 weeks, whereas the longest time was in excess of 32 weeks. The quantity of total magnesia hydrated when the expansion had been reduced to 1 percent ranged from 83 to more than 97 percent.

In general, the lime putties requiring the longest aging periods to effect a reduction in expansion to 1 percent also gave the highest expansions for a given percentage of unhydrated MgO.

The hydrated limes which gave expansion values of 14 percent or more when tested on the "as received" basis required 14 weeks or more of aging as a putty before the expansions were reduced to 1 percent.

Variations in rates of hydration and in expansive characteristics were interpreted as a function of the quantity and the reactivity of the unhydrated magnesia. The autoclave test was suggested as a possible method for checking the degree to which a dolomtic lime had been overburned during the calcining process.

The average percentages of total magnesia hydrated in the putties after aging 1, 3, and 7 days were only 22.5, 29.2, and 41.1, respectively, and the corresponding average percentages of linear expansion of the cement-lime putty bars were 11.0, 10.6, and 9.7, which values are far in excess of the proposed specification limit of 1 percent.

It is evident that the customary soaking of a putty for 1 day on the job hydrates but little MgO in a regularly hydrated dolomitic lime (also known as type N—normal finishing hydrated lime) and leaves the putty still potentially unsound. Even 7 days of soaking is entirely inadequate. In fact, it would be most difficult to specify the time of aging required to reduce the expansion to 1 percent, because the value might range from a minimum of 3 weeks to over 32 weeks. If a specification is to include all of the dolomitic finishing hydrated limes of this type, there would be required about 7 to 8 months—an aging period altogether too long from a practical standpoint.

Considering the fact that the use of regularly hydrated dolomitic lime has resulted in widespread white-coat plaster failure [1] and that this lime cannot be rendered sound within a reasonable soaking period, the question naturally arises as to what suitable alternates are at hand.

Certain manufacturers are now producing a more completely hydrated dolomitic lime. In most instances this has been accomplished by using autoclaves to hydrate the lime at elevated temperature and pressure. Specifications have been formulated which will exclude all hydrated limes containing an undesirably high percentage of unhydrated oxides. They state that the total free calcium oxide (CaO) and magnesium oxide (MgO) in the hydrated product shall not exceed 8 percent by weight (calculated on the "as received" basis) [7]. In the specifications of the American Society for Testing Materials such lime is designated as type S (special) hydrated lime [14]. It is recommended that the consumer insist upon a lime meeting the 8-percent requirement. The new type of lime is marketed in bags carrying an identifying statement.

An accelerated performance test would be preferable to a limitation of the chemical composition. An autoclave test for soundness with a limit of 1.0 percent has been proposed [3]. But until this soundness test or a modification thereof is adopted, the best safeguard for the cosumer is the 8-percent limitation on unhydrated oxides.

Although most high-calcium hydrated limes are not highly plastic, nevertheless, they are used for plastering and masonry construction. They are characterized by having low percentages of unhydrated oxides and low percentages of autoclave expansion, and, consequently, are eminently sound [3].

Another alternate is the use of quicklime because a satisfactory lime putty that is completely hydrated can be obtained from quicklime. It is recommended that the directions for slaking, as given in Standard specifications for gypsum plastering, issued by the American Standards Association as A42.1–1950 [15], be followed.

The authors express thanks to R. L. Blaine and H. J. Valis for determining the surface areas of the 18 hydrated limes by the nitrogen adsorption method and also to J. M. Cameron for his statistical analysis of the relation between the surface areas and the linear expansions of cement-lime bars prepared from these limes.

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WASHINGTON, July 23, 1951.

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